Absolute Photoabsorption Measurements of Molybdenum in the Range 60 to 930 eV for Optical Constant Determination

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INTRODUCTION

In recent years there has been increased interest in the optical properties of Mo in the extreme ultraviolet (EUV)/soft x-ray region, due to its implementation as the absorber layer for Mo/Si and Mo/Be multilayer mirrors. These optics are becoming essential elements in applications such as lithography, astronomy and synchrotron research; they operate at energies below the Si $L_{2,3}$ edge (99.8 eV) and the Be K edge (111.5 eV) respectively, where silicon and beryllium exhibit low absorption. Information on the dispersive and absorptive behavior of each material can be obtained from the real and imaginary part of the energy dependent refractive index $n = 1 - \delta + i\beta$, which has to be measured to a great degree of accuracy. A comprehensive compilation of published data for Mo was published [1] by Henke, Gullikson and Davis in 1993 and will be referred to as the "1993 atomic tables" throughout this abstract. These tables use interpolations between all published experimental data for the absorption (for all elements with atomic number $Z = 1$ to $Z = 92$) combined with a theoretical model [2], in order to determine the imaginary part of the refractive index in the range 10 - 30,000 eV. The real part is then calculated through dispersion (Kramers-Kronig) analysis. It should be noted that the values for n in these tables have been determined according to the independent atom approximation, in the long wavelength and/or small scattering angle regime. The optical constants δ, β of Mo from the 1993 tables are tested for accuracy and self-consistency through a series of sum rules. This evaluation reveals inaccuracies originating in the quality of experimental results. For instance, reflectance data included in the 1993 tables may have been severely influenced by surface oxide, contamination and roughness, in the EUV and soft x-ray regions. New transmission measurements for the refractive index of Mo are presented in this work, in the region of interest for EUV applications. The new compilation of optical constants is evaluated through a series of sum rules and applied in the calculation of the Bragg reflectivity of multilayer optics.

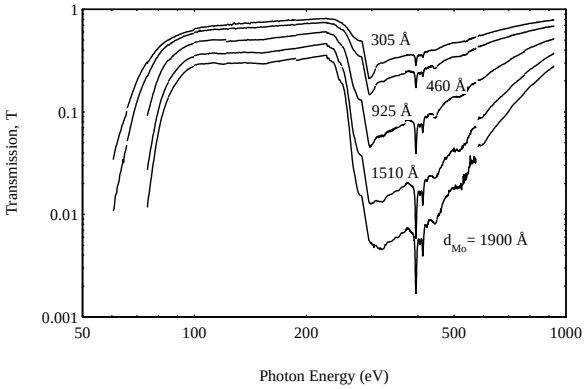

Figure 1. Transmission data from the five C/Mo/C films are shown, corresponding to molybdenum layers of 305, 460, 925, 1510 and 1900 Å each, deposited between two 145 Å thick carbon layers.

SUM RULES

The accuracy of a set of optical data from $\omega = 0$ to $\omega = \infty$ may be tested through the sum rules

$$Z^* = \frac{2}{\pi}\frac{m\epsilon_0}{n_a e^2}\int_0^\infty u\ A_i(u)\ du \qquad i = 1, 2, 3, \tag{1}$$

where the optical data are obtained in one of the following forms: $A_1 = \epsilon_2$, $A_2 = \beta$, $A_3 = Im\{-\epsilon^{-1})\}$ (the "energy-loss function"). $\epsilon = n^2 = \epsilon_1 + i\ \epsilon_2$ represents the dielectric

function of the material and Z^* is the atomic number reduced by the relativistic correction $(Z/82.5)^{2.37}$. For materials with well separated absorption levels, Eq. (1) may be written in its partial form

$$N_{eff,i}(\omega) = Z^* - \frac{2}{\pi}\frac{m\epsilon_0}{n_a e^2}\int_\omega^\infty u\ A_i(u)\,du, \qquad i = 1,2,3, \tag{2}$$

where the quantity under the integral is known as "oscillator strength" and $N_{eff,i}(\omega)$ represents the effective number of electrons contributing to the absorption up to frequency ω. For the energies above the first core absorption level of the material, all 3 sum rules should give identical results. At the lower energies, below the first core absorption level, it is expected from the theory that $N_{eff,1} > N_{eff,2} > N_{eff,3}$. The reason for this behavior is that, for the valence electrons, each of $A_{1,2,3}$ is subject to a different degree of "shielding" from the polarizable background of the core states [3]. At $\omega = 0$, if accurate optical constants are used, Eq. (2) should give $N_{eff,1}(0) = N_{eff,2}(0) = N_{eff,3}(0) = 0$. Eq. (2) yields identically $N_{eff,1}(\infty) = N_{eff,2}(\infty) = N_{eff,3}(\infty) = Z^*$ regardless of the accuracy of the data. The sum rule for $A_2 = \beta$ can be used to characterize absorption data only, while A_1, A_3 involve both real and imaginary parts of the refractive index. Thus, it is often useful to plot all 3 $N_{eff,i}$s of Eq. (2) in order to assess the self-consistency of a set of optical constants. $N_{eff,2}(\omega)$ for Mo was calculated and it was found that 2.3 electrons are missing from the absorption values for Mo in the 1993 atomic tables. The errors in the experimental absorption data are most likely to come from the EUV range, where measurements are particularly difficult and sensitive, as explained in the Introduction. The EUV includes the region around 100 eV, where the optical constants of Mo are of particular importance for multilayer mirror applications.

EXPERIMENT

C/Mo/C free-standing foils were fabricated by sputtering on photoresist coated Si wafers. Five different thicknesses of Mo were deposited, ranging from 305 Å to 1900 Å and the C layer thickness was maintained the same (≈ 145 Å) for all five samples. Prior to removal, Mo layer thicknesses were verified to an accuracy of ± 2% by fitting Cu K_α (8047.8 eV) and Al K_α (1486.7 eV) reflectance data. Fitting was not possible for the 1900 Å sample, due to low visibility of the interference fringes. The C thickness was fitted to values between 140 and 145 Å. For the removal process, support rings were attached to the sample surface using an acetone resistant glue, and the foils were removed by soaking in acetone, resulting in free-standing films with an open area of 7 mm^2. Transmission measurements on the five C/Mo/C foils were performed at beamline 6.3.2., in the energy range 60 - 930 eV, as shown in Fig. 1. The results were fitted for the absorption coefficient μ (cm^2/g) of Mo at each energy, using the expression

$$T = T_0\, e^{-\mu\rho x}, \tag{3}$$

where $T = I/I_0$ is the measured transmission (I, I_0 are the transmitted and incident intensities respectively), ρ = 10.22 g/cm^3 is the Mo density and x is the Mo thickness in the foil. T_0 represents the transmission from layers of other materials present in the foil (in this case the two layers of carbon). Thus, the fitting procedure yields μ and T_0 at each energy. An analysis of the results for T_0 vs. energy revealed ∼ 2% atomic content of Ar in the samples, coming from the Ar^+ ions in the sputtering chamber. Moreover, the presence of ∼ 400 Å overlayer of photoresist, left from the removal process, was found on the samples. The effect of any overlayers is included in T_0 and therefore cancels out in the fitting procedure for the absorption coefficient of Mo, as explained above.

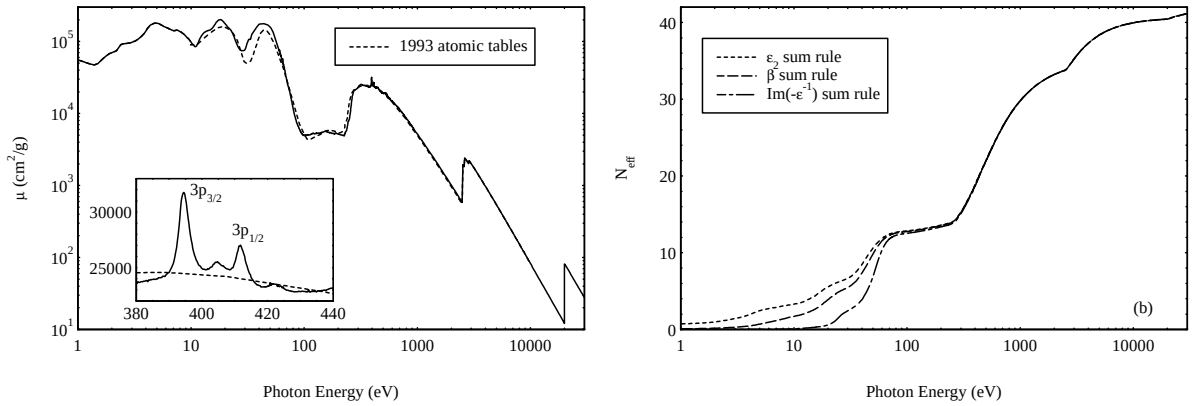

Figure 2. Left: A new compilation of data for μ of Mo from 1 eV to 30 keV is shown with the solid line. The values in the range 60 - 930 eV are obtained from the present measurements. Data from previous workers, compiled in Ref. 4, are used in the low energy region (1 - 35 eV). In the rest of the spectrum, the values of the 1993 atomic tables are used with small corrections around the energy region of the present work. In the inset, the molybdenum $M_{2,3}$ structure and its deviation from the smoothed tabulated values are shown in detail. Right: The sum rules for ϵ_2, β, Im$\{-\epsilon^{-1}\}$ are shown, calculated using the new compilation of optical constants for Mo. The results demonstrate accuracy and self-consistency.

RESULTS AND DISCUSSION

The absorption coefficient μ for Mo derived from the measurements in this work in the energy range 60 - 930 eV is plotted in Fig. 2 (left), combined with the tabulated values [1] and experimental data at the low energies [4] in order to form a set of values for the absorption in the complete spectrum (1 - 30,000 eV). In the inset, it is shown that the structure due to the splitting of the Mo $3p_{1/2}$, $3p_{3/2}$ peaks, which was absent from the simplified calculations in the 1993 atomic tables, is revealed in the new absorption measurements. In the region of operation of Mo/Si normal incidence mirrors (around 92.5 eV, or 13.4 nm in wavelength units), the new experimental data yield lower values for the absorption, while at the Mo/Be mirror regime (around 109 eV, or 11.4 nm), the new values for the absorption appear higher than the 1993 atomic tables. The imaginary (absorptive) part β of the refractive index was obtained in the energy range 1 - 30,000 eV, through the expression $\beta = \mu(\lambda\rho/4\pi)$. Then, δ was calculated from the Kramers-Kronig relations, using the above set of absorption data. The sum rules with the revised set of optical constants for Mo are shown in Fig. 2 (right). The result of the sum rule for β at $\omega = 0$ is $N_{eff,2}(0) = 0$. This demonstrates that the new set of absorption data is accurate, as opposed to the missing oscillator strength of 2.3 electrons found in the absorption values from the 1993 atomic tables. All three $N_{eff,i}$s fall off at the low energies as predicted by the theoretical model discussed in the Sum Rules section. Finally, the Bragg reflectivities for typical Mo/Si and Mo/Be multilayer mirrors for EUV lithography were calculated vs. wavelength, in Fig. 3. It is shown that the new set of data yields 2% higher theoretical peak reflectivity for Mo/Si at 13.4 nm, compared to the 1993 atomic tables. The calculated reflectivity for Mo/Be mirrors with the revised data becomes a few percent lower, for wavelengths longer than the Be edge. These results become significant when one attempts to fit experimental results for the reflectance of a multilayer optic to a theoretical model. Two different sets of optical constants would yield two different sets of fitted parameters (multilayer period, ratio of Mo thickness in the period, interfacial roughness, etc.) for the mirror. Thus, using accurate optical constants is essential for the understanding of the experimental conditions during the multilayer deposition and the prediction of the mirror performance.

CONCLUSIONS

Precise transmission measurements in the range 60 - 930 eV for the determination of the optical constants of molybdenum are presented in this work. Compared to the 1993 tables, the new

results yield different values for the absorption of Mo in the wavelength range 11 - 14 nm, which is important for normal incidence Mo/Be and Mo/Si multilayer mirror applications; the new measurements also reveal the fine structure in the absorption coefficient of Mo around the $M_{2,3}$ edge. Sum rule tests show that the missing oscillator strength from the absorption coefficient in the 1993 tables is recovered and that the new set of optical constants is self-consistent. The results presented have been published [5] and have been used to revise the optical constants files for Mo, which are available on the World Wide Web [6].

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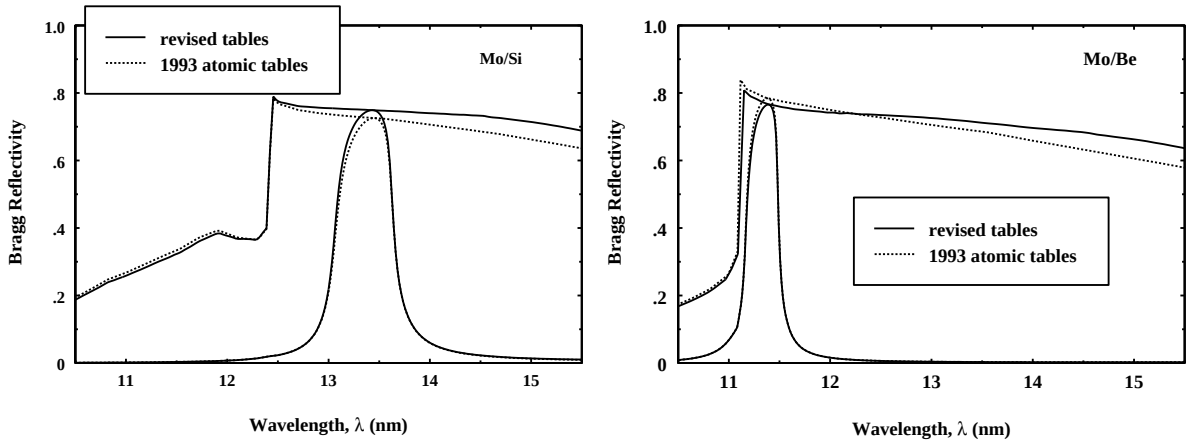

Figure 3. Calculated peak (Bragg) reflectivities at normal incidence, for an infinite multilayer stack of Mo/Si (left) and Mo/Be (right), plotted vs. wavelength. The ratio of Mo thickness to the multilayer period was 0.4 and the period was optimized at each wavelength. The Bragg peak is shown in detail for a Mo/Si mirror with 6.87 nm period (left) and a Mo/Be mirror with 5.75 nm period (right). For comparison, the same calculations are performed using the optical constants in the 1993 atomic tables.

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